

## Electroinitiated and Chemical Copolymerization of Acrylic Acid and Acrylamide in Aqueous System

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### ABSTRACT

The electro – initiated copolymerization of acrylic acid (AA) with acrylamide (Am) occurs by using  $\text{NaNO}_3$  as supporting electrolyte in aqueous system anodically. The with Am seems to be copolymerized, possibly by a free radical mechanism. To support this result, the copolymerization of AA with Am also observed with  $\text{HNO}_3$  initiator in aqueous medium, where gel copolymers, like electrolytically, have been formed via free possibly radical mechanism.

**Keywords:** Electro – initiated copolymerization, chemical copolymerization, AA with Am,  $\text{NaNO}_3$  supporting electrolyte,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$  initiator.

### INTRODUCTION

In literature<sup>1-4</sup>, it was reported that the electrolysis of acrylamide in N, N – dimethylformamide containing  $\text{NaNO}_3$  as supporting electrolyte results in the formation of soluble polymers in the catholyte and of insoluble polymers in the anolyte. The polymerization occurs simultaneously in both compartments. This paper describes our preliminary results of polymerization of acrylic acid in the presence of acrylamide both electrolytically and chemically by  $\text{HNO}_3$ .

### EXPERIMENTAL PART

**Materials:** Water was purified by the usual procedure. AA, Am,  $\text{HNO}_3$

were taken reagent grade and used without purification.

**Polymerization:** The experimental procedure for the electroinitiated polymerization was the same as describe in the previous papers<sup>5-8</sup>. For the chemical polymerization, initiated by  $\text{HNO}_3$ , the reaction mixture 20 ml containing known amount of AA and Am with the initiator were taken into a glass vial which was tightly Stoppard and thermostated. After a given period of time the reaction mixture was poured into a large volume of precipitating reagent (e.g. methanol) to precipitate the polymer which was filtered, dried in an air – oven and weighed.

## RESULTS AND DISCUSSION

When a mixture of AA with Am was electrolysed into H<sub>2</sub>O containing NaNO<sub>3</sub> as supporting electrolyte, the polymerization takes place. The yields of copolymer obtained with different feed ratios of the monomers at a constant current of 30 mA for 240 min electrolysis are presented in Table (1, 2). The copolymers were not analysed for the content of each monomeric unit. The copolymerization of AA with Am proceeds homogeneously because no polymer precipitations take place during the course of reaction. The polymer formed from a mixture of AA and Am are soluble in water at lower feed ratios where as at higher feed ratios it becomes gel. The discharge of NO<sub>3</sub><sup>-</sup> ions is the primary anodic reaction leading to the formation of NO<sub>3</sub><sup>•</sup> radicals, which appear to cause the anodic polymerization. Thus AA with Am seems to be copolymerized possibly by a free radical mechanism.

The copolymerization of AA with Am initiated by HNO<sub>3</sub> in H<sub>2</sub>O was also

carried out. It is quite similar to the electrolytically copolymerized of these two monomers. The reaction mixture remains transparently homogeneous and becomes viscous during the course of reaction, from which the polymer is precipitated in precipitating reagent in cold condition. The effect of feed ratios of the monomers, initiator concentration and reaction temperature on the copolymers yield are shown in Table (3,4,5) respectively. The rise of reaction temperature increases significantly the copolymer yield as obvious from Table (4) and decreasing the time of gelation.

It is to be noted that HNO<sub>3</sub> initiated polymerization of AA (in the absence of Am) gives pale yellow polymers gel and that of Am results in colourless gel during the course of reaction corresponding to the observation in case of their electro – initiated homopolymerizations.

Further detailed studies on the electro – lytically as well as acid (e.g. HNO<sub>3</sub> and HClO<sub>4</sub>) initiated copolymerizations of AA with Am are in progress.

**Table – 1**  
**Electro – initiated copolymerization of acrylic acid (AA) and acrylamide (Am) at their different feed ratios; aqueous solution of NaNO<sub>3</sub> used as supporting electrolyte <sup>a)</sup>**

Feed composition		Electrolyte colour	Polymer yield	
Weight of Am in g	Weight of AA in g		In g	In %
1.000	1.062	Colourless	Nil	Nil
2.000	2.124	Pale Yellow	0.124	3
3.000	3.186	Light Orange	0.248	6
4.000	4.248	Orange	0.400	10
1.000	3.186	Colourless	Nil	Nil
3.000	1.062	Colourless	0.100	2
6.000	2.124	Light Orange	0.600	8

**Condition:**

[NaNO<sub>3</sub>] = 0.235mole/l

Current = 40 mA

Time of electrolysis = 240 min  
 Temperature = 30°C  
 Total volume of Solution = 20 ml  
 Electrodes – St. Steel – St. Steel

Table – 2

Electro – initiated copolymerization of acrylic acid (AA) and acrylamide (Am) at their different feed ratios; aqueous solution of urea nitrate (UN) used as supporting electrolyte <sup>a)</sup>

Feed composition		Electrolyte colour	Polymer yield	
Weight of Am in g	Weight of AA in g		In g	In %
1.000	1.062	Colourless	Nil	Nil
2.000	2.124	Colourless	0.120	~2
3.000	3.186	Light Orange	0.200	~5
4.000	4.248	Orange	0.380	>8
1.000	3.186	Colourless	Nil	Nil
3.000	1.062	Light Orange	0.120	2.5
6.000	2.124	Orange	0.500	>8

**Condition:**

[UN] = 0.333mole/l  
 Current = 40 mA  
 Time of electrolysis = 240 min  
 Temperature = 30°C  
 Total volume of Solution = 20 ml  
 Electrodes – St. Steel – St. Steel

Table – 3

Effect of different feed ratios of acrylic acid (AA) with acrylamide (Am) on the copolymer yield, the copolymerization being initiated by HNO<sub>3</sub>\* IN H<sub>2</sub>O

Feed Composition		Colour of reaction mixture	Polymer yield %	Polymerization time in days
Weight of Am in g	Weight of AA in g			
1.000	0.531	Colourless	Nil	90
1.000	1.062	Colourless	Nil	90
2.000	2.124	Pale Yellow	10	15
1.000	3.186	Yellow	6	15

\* [NHO<sub>3</sub>] = 0.238 mole/l

Total volume of Reaction mixture = 20 ml

**Table – 4**  
**Effect on HNO<sub>3</sub> concentration on the copolymer yield <sup>a)</sup>**

[HNO <sub>3</sub> ] mole/l	Colour of reactin mixture	Copolymer yield %	Polymerization in days
0.079	Colourless	Nil	105
0.158	Colourless	Traces	90
0.237	Pale Yellow	10	15
0.316	Yellow	6	7

**Condition:**

[AA] = 2.124 g

[Am] = 2 g

Volume of reaction mixture – 20 ml

Temperature = 30°C

Precipitating reagent  $\longrightarrow$  CH<sub>3</sub>OH

**Table – 5**  
**Effect of reaction temperature on the copolymer yield <sup>a)</sup>**

Temp. in °C	Polymer yield		Colour of reaction mixture	Polymerization time in hrs.
	In g	In %		
25	Nil	Nil	Colour less	8
35	2.00	32	Colourless (Viscous)	8
45	2.25	35	Colourless (Viscous)	6
55	Gel		Colourless gel	5

**a) Condition:**

Amount of Am = 2.000 g

Amount of AA = 2.124 g

[HNO<sub>3</sub>] = 0.238 mole/l

Volume of solution = 20 ml

Precipitating reagent  $\longrightarrow$  CH<sub>3</sub>OH**REFERENCES**

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